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Why can the activation volume of the cycloadduct decomposition in isopolar retro-diels-alder reactions be negative?

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Abstract

Rate constants of the Diels-Alder cycloaddition reaction of anthracene with tetracyanoethylene, enthalpy of solution of reactants and adduct, enthalpy of the reaction in solution, enthalpy and entropy of activation of the forward and retro-Diels-Alder reactions were determined in 14 solvents. Temperature and pressure effects on the rate of the decomposition of the adduct formed from 9-chloroanthracene and tetracyanoethylene were studied. Since the électrostriction effect can be excluded from the consideration of the isopolar Diels-Alder reaction, negative values of the activation volume in the retro-Diels-Alder reactions can be caused by the different possibilities of penetration of the solvent molecules to large steric branched structures of the transition states and adducts. © 2009 Wiley Periodicals, Inc.

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